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Report 2285

CHEMICAL IONIZATION MASS SPECTROMETRY

OF NITROAROMATIC VAPORS

by
Charles I. Collins

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The negative ion chemical ionization mass spectra for nitroaromatics using a Townsend discharge ion source are reported. The chemical ionization spectra were determined in the presence of various reagent gases and at various temperatures. A sensitivity study of a chemical ionization mass spectrometry system is included which compares detection limits for nitroaromatic compounds in both positive and negative ion detection modes and provides quantitative data on the detection limits for these

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and other compounds. These studies illustrate the ability of negative ion chemical ionization mass spectrometry to provide two or three orders of magnitude increase in specific ion current for compounds containing electronegative functional groups. The sensitivity observed in case of nitroaromatics is useful for detection of parent ions and also permits the observation of other ions and their relationship in terms of changes in internal energy.

The finding that certain organic molecules will capture low-energy electrons (i.e., less than 1 eV) to form negative ions is expected to be of general interest, since this is a very low energy form of radiation interacting and producing profound changes in organic molecules. Of the types of radiation which interact with organic molecules, low-energy electrons are perhaps the least studied.

PREFACE

Information in this report is the result of experimental work done under contract by the University of Virginia. The contract was with the Mine Detection Division (Mr. Robert L. Brooke, Chief), Countermine Laboratory (Mr. Richard R. Rogowski, Chief). Mr. Charles I. Collins was the Technical Monitor. Dr. Donald F. Hunt was the principal investigator.

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METRIC CONVERSION FACTORS
Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol

LENGTH

Symbol	When You Know	Multiply by	To Find	Symbol
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km

AREA

Symbol	When You Know	Multiply by	To Find	Symbol
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha

MASS (weight)

Symbol	When You Know	Multiply by	To Find	Symbol
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	metric tons	t

VOLUME

Symbol	When You Know	Multiply by	To Find	Symbol
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	L
pt	pints	0.47	liters	L
qt	quarts	0.95	liters	L
gal	gallons	3.8	liters	L
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3

TEMPERATURE (exact)

Symbol	When You Know	Multiply by	To Find	Symbol
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

* 1 in = 2.54 cm (exactly).

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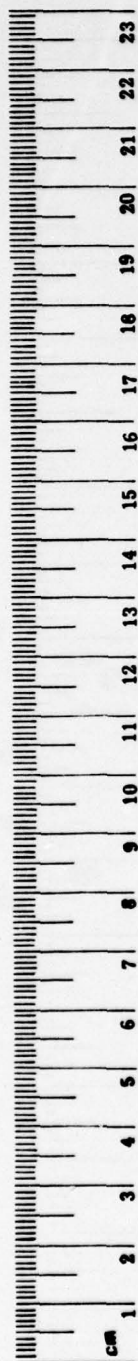
Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
AREA				
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10 000 m^2)	2.5	acres	
MASS (weight)				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	metric tons (1000 kg)	1.1	short tons	
VOLUME				
ml	milliliters	0.03	fluid ounces	fl oz
L	liters	2.1	pints	pt
L	liters	1.06	quarts	qt
L	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
TEMPERATURE (exact)				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

°F
-40   0   32   40   80 98.6 120   160   200   212
-40   -20   0   20   40   60   80   100
°C   37   °C

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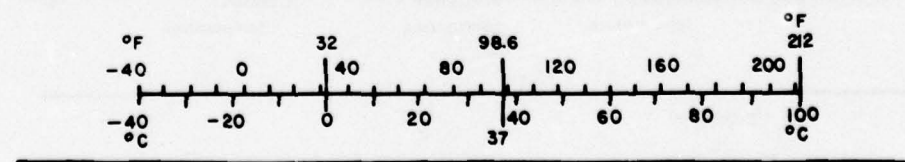
CHEMICAL IONIZATION MASS SPECTROMETRY

OF NITROAROMATIC VAPORS

I. INTRODUCTION

1. **Objectives.** This research was conducted to:

    a. Modify a Finnigan Corp. quadruple mass spectrometer to record positive and negative ion chemical ionization mass spectra simultaneously.

    b. Modify a Finnigan Corp. quadruple mass spectrometer to accept a Townsend discharge chemical ionization (TDCI) ion source.

    c. Investigate the ionization of various nitroaromatic (including trinitrotoluene (TNT), dinitrotoluene (DNT), and mononitrotoluene (MNT)) compounds by negative ion chemical ionization (NICI) mass spectrometry using a TDCI ion source.

    d. Determine chemical ionization (CI) spectra in the presence of various reagent gases and at various source temperatures.

    e. Determine the limits of detection for vapors of the above compounds using NICI mass spectrometry.

2. **Purpose.** The purpose of this research document is to report on NICI mass spectra for several nitroaromatic compounds (TNT, DNT, and MNT) using a TD ion source together with a preliminary study on the use of various reagent gases. A relative sensitivity study using Pulsed Positive Negative Ion Chemical Ionization (PPNICI) techniques to compare relative sensitivities in the positive and negative ion detection mode for these compounds is also discussed. Finally, a quantitative determination is made of the detection limits for TNT vapor using external auxiliary assistance.

3. **Background.** NICI mass spectrometry represents a new technique for use in the qualification and identification of chemical compounds. NICI mass spectrometry probably represents a possible analytical approach to the problem (close to the source) of landmine detection. Through the use of more efficient ionization, mass separation, and detection system, the analysis of trace amounts of certain volatile compounds by NICI have received increased popularity, since its initial development a decade ago. Analysis of very low levels (picogram range) of material has been reported.

NICI mass spectrometry is more sensitive and versatile than conventional electron impact (EI) mass spectrometry (impact conditions: 40 to 80 eV and source pressure in the range 10^{-5} to 10^{-7} torr). First, in EI mass spectrometry most workers report a thousandfold decrease in sensitivity due to inefficiency of electron capture processes for most organic molecules. Put simply, fewer ions are produced (mostly ion-pair formation). This is true since all organic molecules have electrons which can be removed by electron bombardment to produce a positive ion, but not all organic molecules have a high affinity for the addition of an electron. Due to the above problem, the molecular ions are absent from the spectra of the majority of organic compounds. Also an abundance of low-mass fragment ions such as O^-, OH^-, CNO^-, etc.[1][2][3][4][5] clutter the spectra. Second, whereas in EI mass spectrometry the spectra obtained usually require energies above 10 eV, the spectra observed in NICI mass spectrometry are frequently found to be highly dependent on the energy range 0 to 15 eV. This is caused partially by the variety of electron capture processes which are involved in the formation of negative ions.

The three types of processes forming negative ions are: resonance capture (Equation 1), dissociative resonance capture (Equation 2), and ion-pair formation (Equation 3). The equations are as follows:

$$AB + e \rightarrow AB^- \tag{1}$$
$$AB + e^- \rightarrow A. + B^- \tag{2}$$
$$AB + e \rightarrow A^+ + B^- + e \tag{3}$$
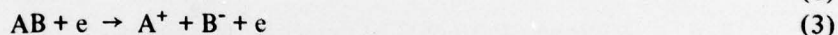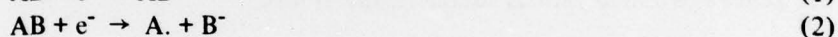
In addition, above 20 eV the beam of electrons will produce positive ions (which will not be observed) and two electrons.

$$AB + e \rightarrow A\text{-}B^+ + 2e$$
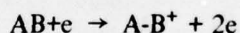
The secondary current is no longer well defined in energy. Hence, if one wants to know the energy dependence of a negative ion mass spectrum, one is limited to electron beam energies below 20 eV (preferably below 15 eV).

Regardless of the above-mentioned problems, EI mass spectrometry has found limited use in the analysis of certain classes of compounds.

[1] J. H. Bowie and B. D. Williams, "MTP International Review of Science, Physical Chemistry, Series Two," Vol. 5, A. Maccoll, Ed., London, Butterworth, 1975, pp 89-127.

[2] J. G. Dillard, *Chem. Rev.*, *73*, 589 (1973).

[3] M. von Ardenne, K. Steinfelder, and R. Tummier; "Electro-nenanlagerungs – Massenspektrographic Organischer Substanzen," New York, Springer-Verlag (1971).

[4] A. L. Burlingame, B. J. Kimble, and P. J. Derrick; *Anal. Chem.*, *48*, 368R (1976).

[5] R. T. Alpin, H. Budzikiewicz, and C. Djerassi; *J. Am. Chem. Soc.*, *87*, 3180 (1965).

In an effort to extend the utility of the EI negative ion technique, Bowie has explored the possibility of tagging complex organics with efficient electron capture groups.[6] Derivation of sample molecules in this manner increases the cross section for capture of the small number of thermal electrons in the ion source and also widens slightly the energy range of electrons that can be captured by the sample without inducing fragmentation. Accordingly, the method enhances the yield of structurally informative anions produced from organic samples. Research in this area also has afforded a wealth of information on the unimolecular fragmentation mechanisms of negative ions. Widespread use of the EI technique in analytical applications is unlikely, however, since much of the ionization still involves interaction of sample molecules with high-energy electrons and occurs by the undesirable ion-pair formation mechanism. The above technique is also several orders of magnitude less sensitive than the methodology described in this report.

Until recently the most useful method of producing negative ion mass spectra was that of von Ardenne[7] who employed a low-pressure (10^{-2} torr) argon discharge to generate a plasma containing positive argon ions and a large population of low-energy electrons. This plasma was constricted by a strong magnetic field and allowed to pass into a chamber containing a gaseous organic sample. Ionization of the sample in this Duoplasmatron source occurs predominantly by the resonance capture and dissociative resonance capture mechanisms, and the resulting spectra exhibit abundant high-mass fragment ions as well as ions characteristic of sample molecular weight. Even though von Ardenne and his coworkers have obtained excellent spectra of hundreds of organic compounds using the above method, the Duoplasmatron ion source has not enjoyed widespread use. This is due in part to the cost and extensive nature of the modifications required to facilitate attachment of the Duoplasmatron source to commercially available mass spectrometers.

It is important to note that the success of the Duoplasmatron source lies in its ability to generate a large population of near thermal electrons, which are readily captured by many organic molecules without inducing extensive fragmentation. A similar population of electrons also is produced when a mass spectrometer is operated under CI conditions. In this method, a reagent gas such as nitrogen at a pressure of 1 torr is placed in the ion source and bombarded with high-energy electrons (100 to 500 eV) in order to generate reagent ions as shown in Equation 4.

$$N_2 + \xrightarrow[\text{electron}]{80\,\text{eV}} N_2^+ + e + N_2 \tag{4}$$

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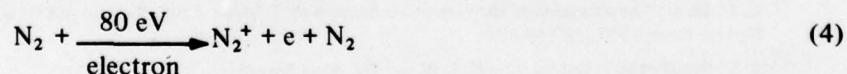
[6] J. H. Bowie and B. D. Williams, "MTP International Review of Science, Physical Chemistry, Series Two," Vol. 5, A. Maccoll, Ed., London, Butterworth, 1975, pp 89-127.

[7] M. von Ardenne, K. Steinfelder, and R. Tummier; "Electro-nenanlagerungs – Massenspektrographie Organischer Substanzen," New York, Springer-Verlag (1971).

Sample molecules are introduced in the usual manner and are ionized by ion-molecule reactions with the reagent ions (Equations 5 and 6).

$$N_2^+ + AB \rightarrow AB^+ + N_2 \qquad \Delta H \simeq -(2\text{-}8eV) \qquad (5)$$

$$N_2 + AB \rightarrow N_2 + AB^+ + e \qquad \Delta H = -(0\text{-}3eV) \qquad (6)$$
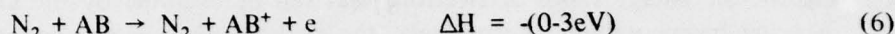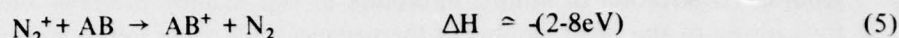
As indicated in Equation 4, the formation of each reagent ion is accompanied by the production of a low-energy electron. Each ionizing event also removes about 30 eV from the bombarding electron[8] which, in turn, undergoes a number of collisions with neutral gas molecules. Consequently, the energy of the incident electron beam is reduced to near thermal values.[9] Thus, operation of a mass spectrometer under CI conditions affords a mixture of positive reagent ions and near thermal energy electrons. Negative reagent ions also can be generated when the reagent gas molecules themselves are capable of forming stable negative ions by the resonance capture or dissociative resonance capture mechanisms.

Considerable effort has been devoted to exploring the analytical potential of various reagent gases for positive ion CI.[10] [11] [12] This is a direct consequence of the finding that the nature of the CI spectrum produced is dependent on both the nature of the reagent gas and the type of ion molecule reaction used to ionize the sample. Different structural information can be obtained from the same sample by recording several positive ion CI spectra using different reagent gases. Similar results should be obtained in negative ion CI studies. Despite this expectation, little research has been conducted on the analytical potential of negative ion CI reagents. Dougherty has reported on the methane and isobutane negative ion CI spectra of polycyclic chlorinated insecticides[13] and aromatic chlorinated pesticides[14] and also has discussed the utility of Cl^- as a CI reagent ion.[15] Use of Cl^- and $O_2^{-\cdot}$ in an atmospheric CI source for the analysis of barbituates,[16] chlorinated aromatics,[17] and highly acidic

[8] C. E. Klotz, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., New York, John Wiley & Sons, 1968, p 40.

[9] E. D. Pellizzari, *J. Chromatogr,* 98,324 (1974).

[10] G. W. A. Milne and M. J. Lacey, "Modern Ionization Techniques in Mass Spectrometry," *Crit. Rev. Anal. Chem.,* 45 (1974).

[11] F. H. Field, "MTP International Review of Sci. Physical Chemistry, Series One," Vol. 5, A. Maccoll, Ed. London, Butterworth, 1972, pp 133-185.

[12] D. F. Hunt, "Applications of the Newer Techniques of Analysis," I. L. Simons and G. W. Ewing, Ed., New York, Plenum Press, 1973, pp 359-376.

[13] R. C. Dougherty, J. Dalton, and F. J. Biros; *Org. Mass Spectrom.,* 6, 1171 (1972).

[14] R. C. Dougherty, J. D. Roberts, and F. J. Biros; *Anal. Chem.,* 47, 54 (1975).

[15] H. P. Tannenbaum, J. D. Roberts, and R. C. Dougherty; *Anal. Chem.,* 47, 49 (1975).

[16] E. C. Horning, M. G. Horning, D. I. Carroll, I. Dzidic, and R. N. Stillwell; *Anal. Chem.,* 45, 936 (1973).

[17] I. Dzidic, D. I. Carroll, R. N. Stillwell, and E. C. Horning; *Anal. Chem.,* 47, 1308 (1975).

compounds[18] [19] also has been reported. The superoxide anion, $O_2^{\overline{\cdot}}$, has been shown to be an excellent reagent for CI analysis of 2-, 3-, 7-, and 8-tetrachloro-dibenzo-p-dioxin,[20] alcohols, and polycyclic aromatic compounds.[21]

II. INVESTIGATION

4.   **Instruments/General.** All spectra were recorded on Finnigan model 3200 or 3300 quadrupole mass spectrometers equipped with standard CI sources. Primary ionization of reagent gas was accomplished using either a Townsend discharge[22] (described in paragraph 7 below) or an 80-eV beam of electrons generated from a heated rhenium filament. Reagent gas and sample pressure was maintained at 0.75-1 torr and 10^{-3} torr, respectively. Source temperatures were in the range 100 to 250°C unless otherwise indicated. Sample introduction was accomplished by one of three procedures. Gases and highly volatile liquids were metered through a Nupro SS-2SG fine needle valve into the reagent gas stream as it passed through an unheated stainless steel inlet line. Higher boiling liquid samples were introduced using a heated 0.5-ml glass bulb connected to a Nupro SS-2SG needle valve. An 18-cm piece of stainless steel tubing inserted in the solid probe port was employed to connect the needle valve to the CI ion source. Solids samples were added in glass capillaries via a direct insertion probe heated independently of the source. To facilitate transport of sample vapor to the site of ionization and to maximize the sample concentration in the ion source, some solid samples were coated on the outside of glass rods protruding from the end of the solids probe.[22] At no time was the sample ion current permitted to exceed 10% of the reagent ion current in either the filament or TD mode of operation. It should be noted that the negative ion sample current becomes saturated if sample sizes larger than 20 ng are employed. This quantity of sample is apparently sufficient to deplete the thermal energy population in the CI source.

5.   **Reagent Gases and Chemicals.** Methane (99.9%) was purchased from Matheson Gas Products, Inc., East Rutherford, New Jersey; nitrogen (ultrahigh purity) and oxygen (USP) were obtained from Air Products and Chemicals, Inc., Allentown, Pennsylvania. Chemicals were acetone and benzoic acid (reagent grade) purchased from local suppliers.

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[18] I. Dzidic, D. I. Carroll, R. N. Stillwell, and E. C. Horning; *J. Am. Chem. Soc.*, *96*, 5258 (1974).

[19] E. C. Horning, D. I. Carroll, I. Dzidic, K. D. Haegele, M. G. Horning, and R. N. Stillwell; *J. Chromatogr.*, *99*, 13 (1974).

[20] D. F. Hunt, T. M. Harvey, and J. W. Russell; *J. Chem. Soc., Chem. Commun.*, 151 (1975).

[21] D. F. Hunt, G. C. Stafford, F. W. Crow, and J. W. Russell; *Anal. Chem.*, *48*, 2098 (1976).

[22] D. F. Hunt, C. N. McEwen, and T. M. Harvey; *Anal. Chem.*, *47*, 1730 (1975).

6. Pulsed Positive Negative Ion Chemical Ionization (PPNICI) Mass Spectrometry. Simultaneous recording of positive and negative ion CI mass spectra[23] on Finnigan models 3200 and 3300 quadrupole mass spectrometers is accomplished by pulsing the polarity of the ion source potential ± 10 V and the focusing lens potential (± 10 V) at a rate of 10 kHz as illustrated in Figure 1. Under these conditions, packets of positive and negative ions are ejected from the ion source in rapid succession and enter the quadrupole filter. Unlike the situation in magnetic sector instruments, ions of identical mass to charge ratio (m/e), but different polarity, traverse the quadrupole field with equal facility and exit the rods at the same point. Detection of the positive and negative ion beams is accomplished using two model 4751 analog continuous dynode electron multipliers (Galileo Electro-Optics Corp., Sturbridge, MA) placed side by side at the exit aperture of the quadrupole rods. The potential on the first dynode is maintained at +1200 to +2000 V on one multiplier and -1200 to -2000 V on the other. Accordingly, positive ions are attracted to one multiplier and negative ions are attracted to the other. The result is that positive and negative ions are recorded simultaneously as deflections in the opposite directions on a conventional light beam oscillograph (LBO). Signals from the positive ion multiplier are handled with standard Finnigan electronics. The negative ion signal is processed by commercially available equipment. This includes a floating coaxial feed-through (Ceramaseal, Inc., New Lebanon Center, NY) and negative ion preamplifier (Extranuclear Laboratories, Pittsburg, PA).

New mass spectrometer pulses positive and negative ions
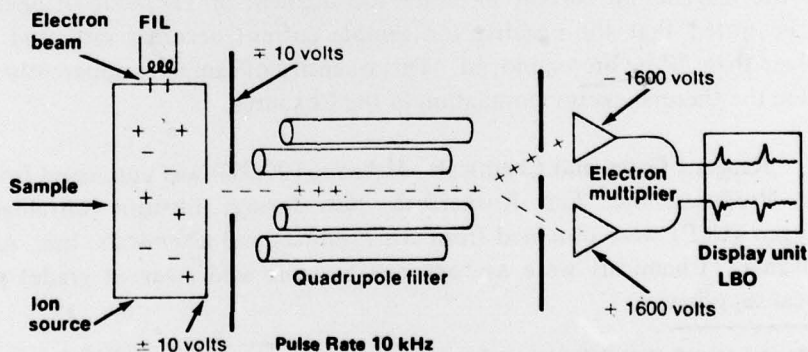
Figure 1. Pulsed positive negative ion chemical ionization mass spectrometer.

[23] D. F. Hunt, G. C. Stafford, F. W. Crow, and J. W. Russell; *Anal. Chem.,* 48, 2098 (1976).

In order to obtain a direct comparison of ion currents produced in the positive and negative ion mode using the PPNICI technique, it is necessary to know the relative gain of the positive and negative ion multipliers. This is accomplished in the present study by inserting a Faraday cup in place of the multipliers and then measuring the positive and negative ion current obtained from an unheated solid probe sample of benzoic acid using 1 torr methane as the reagent gas. Under the above conditions the ratio of $(M-1)^-/(M+1)^+$ is 1:4. This experiment then is repeated with the dual electron multipliers in their standard configuration. Equal gain on the multipliers is achieved by varying the voltage applied to each multiplier until the above ion current ratio for benzoic acid is obtained.

7. **Townsend Discharge CI Ion Source.** To facilitate the use of oxidizing reagent gases, the CI source on the Finnigan 3200 and 3300 quadrupole mass spectrometers was modified to accommodate a Townsend discharge.[24] This was accomplished by mounting a discharge tube in the 1/8-inch hole remaining in the ion chamber walls after the conventional electron trap assembly was removed (Figure 2). Over this hole the following items are placed in order: a nickel screen (85% transmission) (Scientific Instrument and Equipment Division, Bendix Corp., Rochester, NY), a hollow cylindrical insulator formed from machinable glass ceramic (Corning Glass Works, Corning, NY), and a cathode machined from stainless steel. These items are assembled with 0-80 screws insulated with sapphire and ceramic spacers. The cathode of the resulting assembly is then connected through a 3-MΩ (2-watt) current limiting resistor to the negative terminal of a 1600-V power supply. This power supply includes 18 type B, 90-V (Eveready No. 490) batteries connected in series, a variable voltage control, and a meter capable of measuring discharge currents from 1 to 1000 μA.
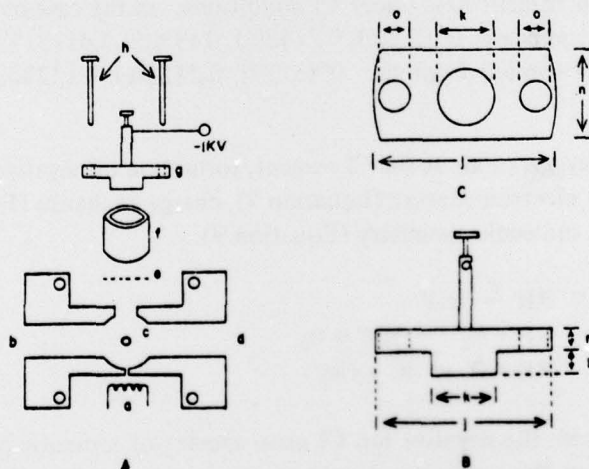
Figure 2. Townsend discharge ion source: (A) Discharge tube components; (B) stainless steel cathode (g) as viewed from the side; (C) stainless steel cathode as viewed from the bottom; (c) ion source volume; (d) solids probe inlet; (e) 85% transmission Ni screen; (f) hollow glass ceramic cylinder i.d. 3/16 inch, o.d. 1/4 inch, length, 3/16 inch; (h) stainless steel screws 0-80 UNF-2A X 3/8 inch; (j) 9/16 inch; (k) 3/16 inch; (l) 1/16 inch; (m) 1/16 inch; (n) 1/4 inch; (o) 3/32 inch.

24 D. F. Hunt, C. N. McEwen, and T. M. Harvey; *Anal. Chem.*, 47, 1730 (1975).

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For operation of the Townsend discharge as a source of electrons (anode mode) to ionize a reagent gas at 1 torr, the voltage between the two electrodes is increased to between 800 and 1200 V until the ion current from the source is maximized. Under the above conditions the TD affords 10 to 30 μA of electron current, is completely stable, and is unaffected by the pulse frequency applied to the ion source and lens for PPNICI experiments.

III. RESULTS AND DISCUSSION

8. Negative Ion CI Mass Spectra of Nitroaromatic Compounds. Negative ion CI mass spectra of TNT, DNT, and MNT molecules have been obtained using four different gases (methane, nitrogen, oxygen, and air) as the CI reagents. Results of these experiments are presented in Tables 1 and 2.

Under CI conditions neither methane nor nitrogen form stable negative ions. Production of positive ions from these molecules, however, is accompanied by formation of a population of near thermal electrons which function as "reagent ions" in these two gases. Negatively charged ions from sample molecules are formed predominately by electron capture in these two reagent gases. Small amounts of OH^- are formed from water as an impurity in the methane and nitrogen, but the reaction of this ion with the sample is seldom responsible for more than a few percent of the negative sample ion current.

In contrast to the above situation, both air and oxygen afford abundant negatively charged reagent ions under CI conditions. In the case of oxygen at 0.8 torr the following ions appear: $O^+(5.2\%)$, $O_2^+(48\%)$, $O^-(3.4\%)$, $OH^-(31\%)$, and $O_2^-(12.5\%)$. The same ions are formed from air: $O^+(5.2\%)$, $O_2^+(25\%)$, $O^-(22\%)$, $OH^-(27.5\%)$, and $O_2^-(20.3\%)$.

With oxygen or air as the CI reagent, formation of negatively charged sample ions can occur by electron capture (Equation 7), charge exchange (Equation 8), and/or Brönsted base ion molecule chemistry (Equation 9).

$$RH \xrightarrow{e^-} RH^{\overline{\cdot}} \tag{7}$$
$$RH + O_2^{\overline{\cdot}} \rightarrow RH^{\overline{\cdot}} + O_2 \tag{8}$$
$$RH + O^{\overline{\cdot}} \rightarrow R^- + OH^{\cdot} \tag{9}$$

In general, the negative ion CI mass spectra of aromatic compounds exhibit high ion currents in the molecular weight region of the spectra. Those fragment ions that form are highly characteristic of structure and correspond to the loss of small moieties such as OH, NO, O, and NO_2. Very little current is carried by the NO_2^- ion

Table 1. Negative Ion Chemical Ionization Mass Spectra of Nitroaromatic Compounds

Reagent Gas	Compound	MW	% Total Sample Ion Current*						
			M⁻	(M-1)⁻	(M-OH)⁻	(M-NO)⁻	(M-O)⁻	NO₂⁻	Other, m/e (%)
1 torr, CH₄	TNT	227	37.6	—	13	26.6	6.7	3.8	181 (5.8) 167 (4.4) 151 (2.1)
	2,4-DNT	182	68.9	—	2.7	17.3	6.4	4.7	—
	o-MNT	137	95.7	—	4.3	—	—	—	—
	m-MNT	137	45.2	—	14.4	—	13.5	26.9	—
	p-MNT	137	69.2	—	8.3	—	10.8	11.7	—
1 torr, N₂	TNT	227	56.8	1.8	19.9	15.6	—	—	181 (1.6) 167 (4.3)
	2,4-DNT	182	86.6	1.6	3.8	5.6	2.4	—	—
	o-MNT	137	100	—	—	—	—	—	—
	m-MNT	137	100	—	—	—	—	—	—
	p-MNT	137	100	—	—	—	—	—	—
0.8 torr, O₂	TNT	227	43.5	29.9	9.8	15.4	1.4	—	—
	2,4-DNT	182	23.9	60.3	—	8.8	5.2	1.8	—
	o-MNT	137	49.6	30.0	—	—	5.0	15.4	—
	m-MNT	137	53.6	22.6	—	—	3.0	13.4	91 (7.4)
	p-MNT	137	35.8	65.1	—	—	2.3	5.8	—
1 torr, Air	TNT	227	66.2	5.0	20	8.8	—	—	—
	2,4-DNT	182	62.5	34.2	1.3	—	2.0	—	—
	o-MNT	137	96.8	—	—	—	3.2	—	—
	m-MNT	137	95.3	4.7	—	—	—	—	—
	p-MNT	137	100	—	—	—	—	—	—

* Ion source temperature 110°C.

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Table 2. High Temperature Negative Ion CI Mass Spectra of Nitroaromatic Compounds

| Reagent Gas | Compound | MW | M⁻ | % Total Ion Current* | | | | | |
				(M-1)	(M-OH)⁻	(M-NO)⁻	(M-O)⁻	NO₂⁻	Other, m/e (%)
1 torr, CH₄	TNT	227	12.1	–	33.2	39.2	–	–	181 (7.8) 167 (7.7)
	2,4-DNT	182	5.2	–	21.6	34.3	–	29.2	135 (9.7)
	p-MNT	137	–	–	–	–	–	100	–
1 torr, N₂	TNT	227	15.5	2.8	36.5	37.5	–	5.8	181 (1.9)
	2,4-DNT	182	41.0	1.8	15.9	27.2	–	11.4	136 (2.7)
0.8 torr, O₂	TNT	227	16.4	9.4	9.4	13.1	–	51.7	–
	2,4-DNT	182	14.0	43.8	2.8	6.7	–	31.0	136 (1.7)

* Ion source temperature, 200°C.

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which dominates negative ion spectra recorded under conventional EI conditions. In addition to the above ions, formation of an M-1 ion occurs when air or oxygen is employed as the CI reagent. All three of the reagent ions, OH^-, O^-, and O_2^-, in these gases are probably sufficiently strong bases to remove protons from the nitroaromatic compounds studied.

Negative ion CI spectra of nitroaromatic compounds were all found to be highly temperature dependent. Increasing the ion source temperature altered the distribution of sample ion currents substantially. As shown in Table 2, spectra of the nitroaromatics recorded at 200°C all exhibit significantly more fragmentation than those recorded at 100°C. The cross section (sensitivity) for ion formation may also vary considerably with temperature, but the necessary experiments to check this have not been performed.

9. Relative Sensitivities in the Positive and Negative Modes for these Compounds. Under CI conditions the negative ion current obtained from nitroaromatics should exceed the positive ion current by a factor of 10^2 to 10^3. This means that by using negative ion chemical ionization (NCI) mass spectrometry the limit of detection for nitroaromatics should be more than a hundred times lower than the detection limit currently realized by conventional EI and positive chemical ionization techniques.

The enhanced negative ion sensitivity predicted above is based on the assumption that positive and negative ions are destroyed in a CI source at the same rate and by the same process (i.e., diffusion of ions to the ionization chamber walls). Formation of positive sample ions under CI conditions requires a collision between positively charged reagent ion and neutral sample molecule. Since this process is diffusion controlled, reactions occurring on every collision usually have rate constants on the order of 10^{-9} molecules cm^{-3}. Formation of negative sample ions by electron capture is also governed by diffusion if the process proceeds with unit efficiency. However, since the mobility of an electron is about 100 times greater than that of an ion, the rate constant for resonance electron capture can be more than two orders of magnitude (10^2) greater than typical ion molecule reaction rate constants. We conclude that formation of negative ions by electron capture can be $> 10^2$ faster than any ion molecule reaction producing a positive ion. If the rate of sample ion destruction is the same for positive and negative ions, the larger rate of formation of negative ions should be reflected in a 100 to 1000 times decrease in sample size required for negative versus positive ion mass spectrometry.

10. Determination of the Limits of Detection for TNT Vapors Using Negative Ion Chemical Ionization Mass Spectrometry (CIMS). The following methods were used:

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a. **Method I – Gas Chromatography Mass Spectrometry (GCMS).** In the initial experiments to determine the lower limit of detection for TNT vapors by negative ion quadrupole CIMS, samples were introduced to the ion source via a gas chromatograph interfaced directly to the mass spectrometer. Acetone solutions containing known concentrations of TNT were used in this work. The signal carried by the molecular anion, $M^{\cdot}$, at mass number (m/e) 227 was sampled continuously by operating the spectrometer in the single ion detection mode and by using a Finnigan PROMIN and Rikadenki recorder to display the signal. The quantity of sample injected into the GC was decreased until the limit of detection (Signal/Noise (S/N) = 2) was achieved. Other pertinent experimental conditions are as follows:

Filament current:		0.2 mA at 100 eV
Source pressure:		0.86 torr of methane
Column:		5 ft by ¼ in. o.d., glass, silylated
Support:		60/80 gas chrom Q
Coating:		silicone ov-1 (methyl) 3%
Carrier gas:		methane
CL reagent gas:		methane
GC column flow rate:		7 ml/min
TNT retention time:		1.25 min
Temperatures:	Injection	275°C
	Column	210°C
	Transfer lines	280°C
	Ion Source	100°C

Using the above methodology, an S/N of 3 was obtained when 1 pg of TNT was injected onto the GC column.

b. **Method II – Use of a Jet Separator.** In a second set of experiments, the GC was disconnected and replaced with a standard Finnigan jet separator open to the atmosphere at one end and interfaced to the ion source at the other. The sample consisted of a large-mouth jar containing air saturated with TNT vapors. The contents of the jar were sampled by placing the open vessel near the open end of the separator for approximately 1 second. Additional experimental parameters are listed below:

Temperatures:	Separator and transfer lines	250°C
	Ion Source:	100°C
Air through separator:		160 ul
Methane added after:		540 ul
Monitored ion:		m/e 227 ($M^{\cdot}$) for TNT
Recorder:		Finnigan PROMIN plus Rikadenki Recorder

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Air saturated with TNT afforded a S/N = 4000 in the above experiment. This result suggests that a level of TNT 2000 times lower than that employed could be detected with a S/N = 2. Since saturated TNT in air corresponds to 3 parts TNT in 10^9 parts of air, the lower limit of detection by this method would appear to be 1.5 parts in 10^{12} or 15 fg/cm^3 of air.

c.   **Method III — Capillary Flow Restrictor.** In a third experiment, the jet separator was removed and replaced with an 0.008-inch glass capillary flow restrictor. Flow of air at 1 atm through this glass capillary produced an ion source pressure of .800 torr. Other experimental conditions were identical to those employed in method II. With the capillary flow restrictor in place, air saturated with TNT afforded a S/N ratio of 2000. This value extrapolates to a detection limit for TNT of 3 parts in TNT in 10^{12} or 30 fg/cm^3 of air.

IV. GENERAL COMMENTS

11. Detection Limits of Other Compounds. The detection limit of TNT achieved using the jet separator and capillary flow restrictor methods is approximately 50 times lower than that obtained in the GCMS experiment. Irreversible sample absorption in the GC could explain the above discrepancy, but the necessary experiments to prove this have not been performed.

It is perhaps worth mentioning that several other compounds have recently been detected at the femtogram level by negative ion GC CIMS. These compounds are shown on the next page along with the lower limit of detection achieved.

Since the cross section for formation of a stable negative ion from TNT is equal to that of the above compounds, we expect a similar lower limit of detection for TNT of about 1 fg/cm^3 of air with S/N = 2 (1 part in 10^{13}), using our present instrument configuration. The level realized to date is 15 fg/cm^3 of air.

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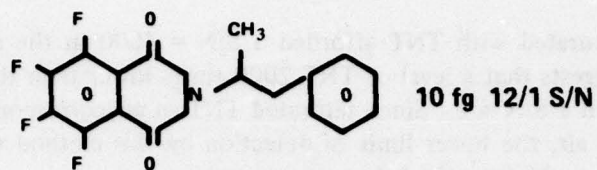
Tetrafluorophthaloyl amphetamine   **10 fg 12/1 S/N**

20 fg S/N 2/1
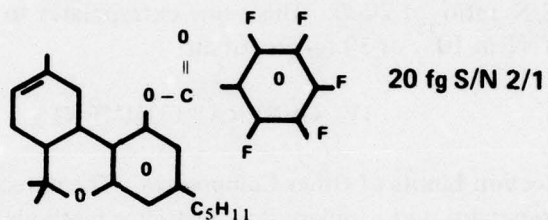
Δ^{16} – **Tetrahydrocannabinol pentafluorobenzoatp**
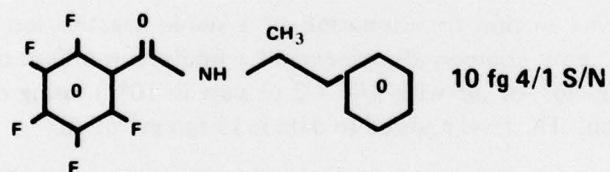
Pentafluorobenzoyl amphetamine   **10 fg 4/1 S/N**

Pentafluorobenzylidene dopamine   **25 fg 4/1 S/N**

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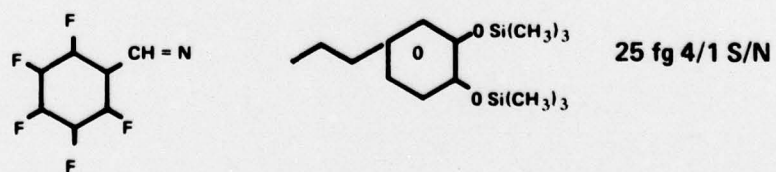| No. Copies	Addressee	No. Copies	Addressee
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